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rent of the gas, mixed with half its volume of marsh-gas, be passed through a stratum of strong solution of ammonia only half an inch deep, not a trace of boric methide escapes absorption.

Ammonia-Boric Methide.

When dry ammoniacal gas is mixed with an equal volume of dry boric methide, both gases instantly disappear, with evolution of a considerable amount of heat, and production of a white, volatile, crystalline compound. The latter is also formed when boric methide is passed into solution of ammonia. The colourless liquid stratum which forms upon the surface soon solidifies when it is placed over sulphuric acid *in vacuo*. A quantity of the compound obtained by this latter process was purified by solution in ether and subsequent recrystallisation. On being submitted to analysis, it yielded results agreeing with the formula—

$$NH_3 + B(C_2H_3)_3.$$

Ammonia-boric methide is deposited from its ethereal solution in magnificent arborescent crystals, which rapidly volatilize without residue when exposed to the air. They possess a caustic and bitter taste, and a very peculiar odour, in which both the smell of ammonia and of boric methide can be recognised. Ammonia-boric methide fuses at 56° C. and boils at about 110° C. In a current of air, or better, of carbonic acid, it sublimes at a very gentle heat, and condenses in magnificent arborescent crystals. Determinations of the specific gravity of its vapour, at three different temperatures, gave the numbers 1·251, 1·258, and 1·250, indicating that the vapour of ammonia-boric methide consists of equal volumes of boric methide and ammonia united without condensation :—

1 vol. Boric Methide . . .	1·93137
1 vol. Ammonia	·5873
	2)2·51867
	1·25933

Thus the formula of ammonia-boric methide is a four-volume formula,* a state of condensation which is usually considered to

* H_2O_2=2 vols.

be abnormal, and which, when it occurs, is generally explained by the assumption of a decomposition of the body at the moment of conversion into vapour. The proof of the disunion or integrity of the vaporous molecule of ammonia-boric methide would be interesting in connexion with these so-called anomalous vapour-densities, but I have to regret my inability to offer any sufficiently decisive solution of this problem. The difficulty to be overcome is the finding of a reagent that will not decompose ammonia-boric methide at elevated temperatures, but which would absorb ammonia only, out of a mixture of this gas with boric methide, at a temperature above the boiling-point of ammonia-boric methide. Chloride of calcium does not decompose ammonia-boric methide; but although it readily absorbs ammonia at ordinary temperatures, it allows the whole of it to escape at 110° C. Chloride of zinc decomposes ammonia-boric methide before the latter volatilizes. The same effect is produced by all the strong acids, which are therefore also inadmissible, whilst dry boracic acid does not absorb ammonia even at ordinary temperatures. The substance which appeared to be best adapted for this reaction was dry and recently fused chloride of copper. This salt does not decompose ammonia-boric methide below the boiling point of the latter, whilst it readily absorbs ammonia, and retains it at a temperature of 160° C. I will now describe the mode in which an experiment with this substance was conducted, and the results which were obtained. A quantity of ammonia-boric methide was introduced into a graduated tube filled with mercury, and inverted in a vessel containing the same metal. The whole was now immersed in an oil-bath, and heat applied until the boron-compound was converted into vapour, the volume of which, at a known temperature and pressure, was then observed. After the apparatus had been allowed to cool, a fragment of chloride of copper was passed up into the tube, and heat again applied. The boron-compound soon melted and enveloped the fragment of chloride of copper: as the temperature approached the boiling-point of ammonia-boric methide, the latter slowly boiled off from the chloride of copper, and the vapour then occupied the same volume as that read off before the introduction of the chloride of copper. The mercury in the tube remained steady for two or three minutes; it then gradually ascended, and the contraction of the vapour-volume continued until it was reduced to exactly one-half, as indicated by the following numbers:—

Corrected volume of vapour before treatment with chloride of copper . .	35·67 cub. centims.
Ditto after treatment with chloride of copper	17·85 cub. centims.

By treatment with chloride of copper, 100 volumes of vapour were therefore reduced to 50·04 vols., and the residue consisted of pure boric methide gas. It is obvious that this absorption may be due either to decomposition of the vapour of ammonia-boric methide *by chloride of copper* at an elevated temperature, or to the decomposition *by heat* of the boric compound into equal volumes of boric methide and ammonia, the latter being then absorbed by the chloride of copper. Unfortunately, the result of the experiment is not sufficiently decisive to compel the adoption of either of these hypotheses, although the formation of the vapour and its existence for a few minutes in contact with chloride of copper favour the first more than the second; thus indicating that the vapour of ammonia-boric methide consists of equal volumes of ammonia and boric methide united without condensation, a result which would harmonize with the very generally observed rule, that when two gases or vapours unite in equal volumes, the volume of the compound is equal to that of its constituents.

Ammonia-boric methide scarcely absorbs a perceptible amount of oxygen at ordinary temperatures, even after several days' exposure to the gas; but it takes fire below 100° C. when heated in contact with the air. Its vapour is also very inflammable; thus, when ammonia-boric methide is placed under the receiver of an air-pump, and the air is being withdrawn, the explosion of the mixture of air and vapour in the cylinders of the pump is frequently determined by the rise of temperature consequent upon the depression of the pistons when the rarefaction has become considerable.

Boric methide is also absorbed by aniline with great avidity. Acids expel the gas from this compound unchanged.

Terhydride of phosphorus has no action upon boric methide. A mixture of equal volumes of the two gases is spontaneously inflammable, burning with a yellowish-white flame, in which the characteristic green tinge attending the combustion of boric methide is no longer perceptible.

Compounds of Boric Methide with Potash, Soda, Lime, and

Baryta.—Solution of caustic potash absorbs boric methide with great energy. The saturated solution, exposed over sulphuric acid, *in vacuo*, dries down to a gummy mass, which scarcely exhibits signs of crystallisation. The same body may be more conveniently formed by decomposing ammonia-boric methide with alcoholic solution of potash, taking care to employ an excess of the former. On evaporation over sulphuric acid *in vacuo*, the excess of the ammonia-compound volatilizes, and is decomposed by the sulphuric acid, with elimination of boric methide: thus the potash-compound evaporates in an atmosphere of boric methide. Nevertheless even by this method I did not succeed in obtaining the potash-compound in a state of purity, potash-boric methide thus prepared yielding on analysis 47·93 per cent. of potash, and 42·86 per cent. of boric methide, numbers only very remotely indicating the formula

$$KO.B(C_2H_3)_3,$$

which requires 45·67 per cent. of potash and 54·33 per cent. of boric methide. The appearance of the compound, even after exposure to gentle heat *in vacuo*, suggested the presence of water, which could not, however, be expelled at a temperature below that at which potash-boric methide itself is decomposed.

Boric methide is also readily absorbed by solution of neutral carbonate of potash, bicarbonate of potash and potash-boric methide being apparently formed. Although boric methide and potash unite with remarkable energy, yet they are separated by acids with the greatest readiness; even carbonic acid in the presence of water can expel boric methide from its potash-compound; thus, if an aqueous solution of potash-boric methide be passed into carbonic acid standing over mercury, the acid gas soon becomes replaced by pure boric methide.

Soda-boric methide, baryta-boric methide, and *lime-boric methide* are similar bodies, produced by the absorption of boric methide gas by caustic solutions of soda, baryta, and lime; they are all readily soluble in water, and react alkaline.

Boric methide in combination with the alkalies and alkaline earths has almost entirely lost its powerful affinity for oxygen; nevertheless, when these bodies are placed in contact with a known quantity of oxygen over mercury for several days, the volume of the gas perceptibly diminishes.

The great difficulty, not to say danger, attending the gradual

oxidation of considerable quantities of a gaseous and spontaneously inflammable body like boric methide, has prevented me from following this compound into its products of oxidation, as was done in the case of boric ethide. With a graduated supply of oxygen, however, boric methide appears to comport itself like boric ethide, and the compounds formed are probably homologous with diethylate and dihydrate of boric dioxyethide.

In conclusion, it can scarcely be doubted that the action upon boracic ether of the zinc-compounds of the remaining alcohol-radicles would produce the homologues of the bodies described in the foregoing pages. It may also be remarked, that the existence of bodies like boric dioxyethide, in which one-third of the oxygen in boracic anhydride is replaced by ethyl, altogether abolishes any supposed analogy between carbonic and boracic acids, whilst it proves that the composition of the latter acid is expressed by the formula BO_3, or some multiple of that formula. I am at present engaged in studying the action of zincethyl and sodium-ethyl upon the ethers of silicic, carbonic, oxalic, and acetic acids.

XLVII.—*On a Method for the Determination of Nitric and Nitrous Acids.*

By A. Vernon Harcourt, M.A., Student of Christ Church, Oxford.

In the course of some experiments upon the alkaline peroxides*, I had occasion to determine the quantity of nitrogen in a mixture of nitrate and nitrite of potassium. Finding no account of a method suitable for this purpose, I was compelled to seek one experimentally. That at which I arrived, and which is briefly indicated in the paper referred to, gives very exact results, and promises to be available for the determination of any nitrate or nitrite whatsover and however admixed.

Since that time a method has been published by Professor

* Journ. Chem. Soc., vol. 16, p. 289.

Schulze,* differing only in one important particular, the employment of platinized zinc in the place of zinc and iron, from that pursued by me. A brief account of this latter method, and its results, may, however, still be acceptable.

It has long been known, that when nitre is heated with an excess of potash, zinc, and water, ammonia gas is evolved. But the conversion effected in this way is incomplete. In a number of experiments made with the view of founding a quantitative method upon this reaction, the ammonia thus formed was collected and determined; it amounted to about $\frac{3}{4}$ths of that quantity, which the weight of nitre used was theoretically capable of yielding. No modification in the proportions of zinc and potash solution, or in the degree of concentration of the latter, materially improved this result. Under no conditions was the relation sufficiently constant to furnish an empirical number. Nitre, heated in a combustion-tube with a mixture of powdered zinc and soda-lime, yielded only a trace of ammonia.

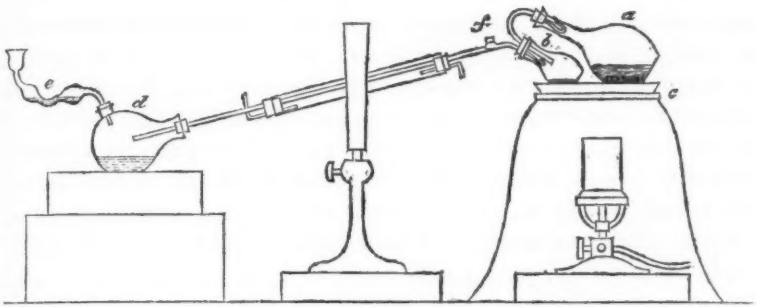
It was observed, I believe, by Mr. Griffin,† that, when a moderately concentrated solution of potash is poured upon a mixture of zinc and iron, hydrogen is freely disengaged, even without the application of heat. This action is electrolytic; the zinc is oxidized, and the hydrogen formed upon the surface of the iron. A similar effect is observed if platinum, copper, or tin, be substituted for iron; but the action with these metals is less energetic. The addition of a nitrate to the mixture evolving hydrogen, is followed by an immediate development of ammonia. This reaction furnishes a good qualitative test of the presence of nitric or nitrous acid. The fluid to be examined is reduced to a small bulk, and poured into a test-tube containing two or three grammes of a mixture of granulated zinc and clean iron filings. A small quantity (5 or 6 c.c.) of strong potash solution is added, and the whole heated to boiling. The usual tests for ammonia may be applied at the mouth of the tube: ·005 grm. of nitre thus treated, gave a distinct reaction with reddened litmus paper. The employment of potassio-iodide of mercury renders this test far more delicate. The mixture should be gently boiled for five or ten minutes, and the evolved gases led into a small quantity of dilute hydrochloric acid. The acid solution is

* Chem. Central Blatt, No. 53.

† Griffin's Chemical Recreations, p. 231.

is supersaturated with potash, and tested with a drop of potassio-iodide of mercury: ·001, ·0005, and even ·0001 grms. of nitre gave a distinct red coloration when thus treated.

The apparatus which I have employed for quantitative determinations is represented, on a scale of $\frac{1}{8}$th, in the following figure.



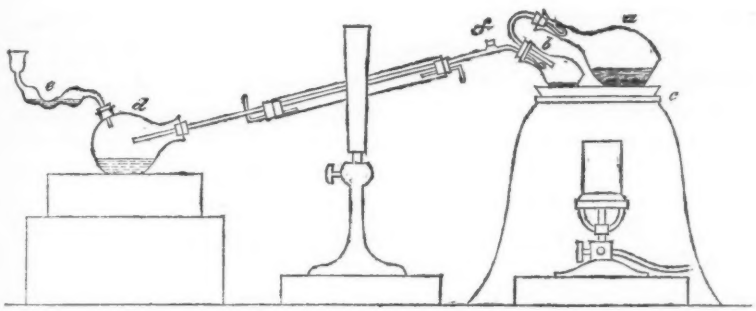
The flask, *a*, which has a capacity of 200 C.C., is designed for the generation of ammonia by the mutual action of nitric acid, zinc, iron, potash, and water. It is connected by a bent tube, drawn out and recurved at its extremity, with the smaller flask or bulb *b*; and the two are so arranged, that they both rest at a considerable angle of inclination upon the sand-bath, *c*. The smaller flask is connected with a condenser which leads into the tubulated receiver, *d*. In the upper part of the condensing tube is a small tubulure *f*, closed during the distillation by a plug of india-rubber. The tube, *e*, which is provided with two or more bulbs and a funnel-head, has the shape indicated in the figure. It is fastened into the tubulure by means of a perforated plug of caoutchouc, which, when slightly greased, makes a tight and supple joint. A standard solution of sulphuric acid is used for the collection and determination of the ammonia. The excess of acid employed is finally determined by means of a standard solution of caustic potash.

The following is the course of the operation:—The funnel-tube, *e*, is brought into a vertical position, by being turned round in the tubulure through half a circle; a quantity of standard acid from a burette is passed through it into the receiver, more than enough to neutralize all the ammonia that can be formed. Some litmus

solution is added to render visible the progress of the action. The funnel-tube is then restored to a horizontal position, and its bulbs filled up to the proper level by a few drops more of the standard acid. The total quantity of acid that has been taken, is now read off upon the burette. The flask *a* is then removed, its tube and cork, together with the smaller flask, which should contain a little water, remaining in position upon the sand-bath. Into it is introduced about 50 grms. of finely granulated zinc, together with half that quantity of iron filings, which have been cleansed by sifting, and ignition in a covered crucible; a weighed portion of the nitrate to be determined is then introduced, with water sufficient to dissolve it; lastly, a measured quantity of a solution of caustic potash, free from nitre, is added, and the flask immediately replaced. It is essential that the quantity of the metals and of the potash employed, should greatly exceed that proportion which is theoretically necessary for the complete conversion of the nitric acid. In my experiments with nitre, I have generally taken about 0·5 grm. of that substance, 20 c.c. of water, and 20 c.c. of a solution of potash, sp. gr. 1·3. Provided the quantity of potash be sufficient, it is immaterial in what degree its solution is diluted, since, in the course of the distillation, it passes through every stage of concentration. It must not be highly concentrated at the commencement of the operation.

Heat is now applied to the part of the sand-bath immediately beneath the larger flask, and the fluid is gradually raised to the boiling point. If the bubbles of air and hydrogen pass at a moderate rate through the bulb-tube, *e*, there is no risk of a loss of ammonia. When distillation has commenced, the lamp is so placed that the water in the smaller flask *b* may also boil gently. The fluid is thus twice distilled in one operation, and the traces of potash which escape from the flask *a*, are effectually retained in the flask *b*. The end of each of the two exit-tubes is drawn out, and bent into a hook for further security. Repeated experiment has proved the sufficiency of this arrangement for keeping back in a slow distillation everything that is not volatile. The quantity of fluid in the flask *b* can be regulated by adjusting the position of the lamp. The distillation, which should occupy from one to two hours, requires only occasional attention. It may be terminated when hydrogen gas, which is evolved in larger quantity as the potash becomes concentrated, has been passing regularly, for five or ten minutes, through the bulb-tube *e*. When the fluid in *e*

has receded, as the apparatus cools, into the inner bulb, the caoutchouc plug is withdrawn from *f*, and a stream of water poured into the condensing tube, to preclude the possibility of ammonia being retained upon any portion of its surface. The tube *e* is then turned round into the vertical position, and water is passed through it two or three times, after which it is removed, and the tubulure of the receiver closed by a cork. Finally, the receiver itself is disconnected, the end of the condensing tube is rinsed externally, and the determination is completed by adding standard alkali from a burette to the fluid in the receiver till a change of colour appears. Collection in hydrochloric acid, and precipitation by choride of platinum, may be substituted, but the volumetric method gives perfectly sharp results.



The zinc and iron which remain in the generating flask need only to be washed with water, with dilute acid, and again with water, to be ready for a second determination. Metals that have once been used, generate hydrogen far less actively than zinc with a bright surface, and freshly ignited iron; but the production of ammonia proceeds as readily with one as with the other. It may be safely assumed, that the presence of any salts, which are without action upon caustic potash, or upon zinc and iron, will not interfere with the reaction upon which this method depends. The experiment was, however, made of mixing weighed quantities of nitre with various proportions of sulphate of potassium and chloride of sodium. The presence of these salts did not affect the result.

For the estimation of nitric acid in other than alkaline nitrates, the separation of the base may, in some cases, prove a necessary

preliminary. I have experimented only with nitrate of barium and nitrate of lead. The former may be determined exactly in the same way as nitrate of potassium, and with equally good results. The carbonate of barium, which separates on adding solution of caustic potash, is, as might be expected, without influence on the reaction. Nitrate of lead exhibits a slight deficiency when thus directly determined. In five experiments, instead of 8·45 per cent. of nitrogen, the following numbers were found—7·78, 7·83, 8·09, 8·28, 8·11. This deficiency is possibly due to an action of dissolved oxide of lead upon the surface of the zinc. It would certainly disappear if the lead were first separated by means of sulphate of potassium.

A few examples of determinations made by this method are given in conclusion.

A solution of pure nitre was made, and of this 10 c.c. were used in each experiment. This quantity evaporated to dryness, left a residue weighing 0·3838 grm. 1 c.c. of the standard acid employed neutralizes an amount of ammonia, containing 0·002084 grm. of nitrogen. In six consecutive experiments, the number of c.c. of this acid required was—

(1). 25·7, (2). 25·3, (3). 25·3,
(4). 25·4, (4). 25·4, (6). 25·6,

of which the mean is 25·45 c.c.: hence the total nitrogen found is 0·05304 grm.; the nitrogen per cent. 13·82; theory requires 13·86.

In eight consecutive experiments, made with the same standard acid, the quantity of nitre taken for each was 0·4986 grm.

The number of cubic centimetres required was,—

(1). 33·15, (2). 32·9, (3). 33·1, (4). 33·2,
(5). 33·05, (6). 33·1, (7). 33·15, (8). 33·2,

of which the mean is 33·1: hence the total nitrogen found is 0·069; the nitrogen per cent. 13·83.

XLVIII.—*On Oxide of Ethylene, considered as a link between Organic and Mineral Chemistry.*

[A Discourse delivered to the Fellows of the Chemical Society of London, June 5th, 1862.]

By M. Ad. Wurtz.

In the year 1795, four Dutch Chemists, Deiman, Troostwyk, Bondt, and Lauwerenburgh, first made the remarkable experiment of bringing together equal volumes of chlorine and olefiant gases, whereby they obtained a liquid compound, still known by the name of "Dutch liquid." This compound is an organic chloride, the dichloride of the diatomic radicle, olefiant gas or ethylene; and its constitution, or rather its mode of formation and most of its chemical properties, show that it may be represented by the formula

$$(C_2H_4)''Cl_2$$

Oxyde of ethylene is the corresponding oxide—

$$(C_2H_4)''O$$

This oxide cannot be formed directly by the action of oxygen on ethylene,* but it is obtained as a derivative of glycol, of which it is the anhydride or ether.

I must here draw attention to the re-actions by which glycol is produced, for they exhibit a remarkable peculiarity, on which I must especially insist. I obtained this body by the action of potash or baryta on diacetic glycol, a compound produced by the action of bromide or iodide of ethylene on acetate of silver, as shown by the following equation:—

$$(C_2H_4)''I_2 + \left\{\begin{matrix}C_2H_3O\\Ag\\Ag\\C_2H_3O\end{matrix}\right\}O_2 = 2AgI + \left\{\begin{matrix}C_2H_3O\\C_2H_4\\C_2H_3O\end{matrix}\right\}O_2$$

Here we see clearly that 2 atoms of silver are removed, and their place supplied by ethylene, which, thus, as it were, rivets

* I have in vain endeavoured to bring about the direct combination of oxygen and ethylene, by heating a mixture of the two gases in the required proportions in a sealed flask containing acetic acid. I hoped to obtain by this method the acetate of ethylene or acetic glycol.

together the residues of the two molecules of acetate, producing diacetic glycol. Polyatomic radicles are indeed especially characterised by the power which they possess of partially encroaching on several molecules belonging to a simple type, and thus joining these molecules together, so as to form a more complex type. Glycol itself, for example, may be supposed to result from the substitution of ethylene for 2 atoms of hydrogen in two molecules of water thus rivetted together:—

$$\left.\begin{matrix}H\\H_2\\H\end{matrix}\right\}O_2 \qquad\qquad \left.\begin{matrix}H\\(C_2H_4)''\\H\end{matrix}\right\}O_2$$

I must not omit to notice here that the general idea just enunciated was first suggested by Professor Williamson,* when he represented sulphuric acid as derived from two molecules of water in which two atoms of hydrogen are replaced by the radicle sulphuryl:

$$\left.\begin{matrix}H\\H_2\\H\end{matrix}\right\}O_2 \qquad\qquad \left.\begin{matrix}H\\SO_2\\H\end{matrix}\right\}O_2;$$

but I believe myself justified in adding that my own researches on the glycols have afforded a tangible representation, and, as it were, an experimental demonstration of this idea, and have served to establish the notion of polyatomic radicles in organic chemistry.

Glycol cannot be dehydrated directly so as to transform it into oxide of ethylene. This transformation is however effected indirectly, by first subjecting glycol to the action of chlorhydric acid, which expels the water and forms chlorhydric glycol, and by then treating this body with caustic potash—

$$C_2H_4O.H_2O + HCl = C_2H_4O.HCl + H_2O$$
$$C_2H_4O.HCl + KHO = C_2H_4O + H_2O + KCl$$

On adding caustic potash to chlorhydric glycol or chlorhydrate of oxide of ethylene, an immediate precipitation of chloride of potassium takes place, accompanied by violent evolution of gas. This gas conducted into a cooled receiver, condenses into a light, transparent mobile liquid, which is oxide of ethylene.

This compound boils at 13·5°. It is miscible in all proportions with water and with alcohol. Like the isomeric body aldehyde, it reduces nitrate of silver, but more slowly.

* Chem. Soc. Qu. J. iv., 350.

Oxide of ethylene is a very plastic compound, which is capable of uniting directly with a host of bodies: with hydrogen to form alcohol; with oxygen to form glycolic acid; with bromine, forming red crystals, consisting of a bromide of oxide of ethylene, having the composition $2C_2H_4O,Br.^2$; with water, to form glycol, and the polyethylenic alcohols; and, lastly, with ammonia, to form oxygenated bases.

These properties taken together show that oxide of ethylene is analogous to certain oxides belonging to the domain of mineral chemistry. To bring out this analogy by the comparison of its constitution and re-actions with those of the mineral oxides in question, is the object of the present lecture.

In the first place, the basic properties of oxide of ethylene may be demonstrated by a very striking experiment. If a concentrated solution of chloride of magnesium be introduced into a flask, together with oxide of ethylene, the flask then sealed, and the whole left to itself for about 24 hours, an abundant deposit of hydrate of magnesia is produced, while chlorhydric glycol (chlorhydrate of oxide of ethylene) remains in solution. The oxide of ethylene has, consequently, displaced the magnesia; and, in like manner, it displaces alumina, ferric oxide, and cupric oxide. It behaves, therefore, like an oxide, and accordingly we represent it as an oxide, expressing its composition by the formula

$$(C_2H_4)''O,$$

in which the ethylene plays the part of a diatomic radicle.

The question now arises: Do radicles of this nature exist among the metals, and are there any metallic oxides which can be compared, as to their constitution, with oxide of ethylene?

With the view of obtaining an answer to this question, we shall compare with oxide of ethylene, the oxides of *barium, strontium, calcium, magnesium, manganosum, ferrosum, zinc, copper, lead, mercury, &c.*, representing them by the formulæ

$$Ba''O,\ Sr''O,\ Ca''O,\ Mg''O,\ Mn''O,\ Fe''O,\ Zn''O,\ Pb''O,\ Hg''O.$$

In these formulæ, the metals are regarded as diatomic, and, as possessing atomic weights double of those which are commonly assigned to them, thus becoming analogous to ethylene, so far as regards their combining capacity. But are we justified in doubling the atomic weights of these metals? We shall endeavour

to show that this view is supported by facts, relying in the first place, on certain physical proofs, and afterwards adducing a certain number of arguments, drawn from chemistry itself, in favour of the opinion that we have adopted. It is right to add that the notion of polyatomic metals was introduced into chemical science by Dr. Odling, and that the idea of regarding the metals above-mentioned as diatomic, and doubling their atomic weights, was first conceived by M. Cannizzaro.

Observe, in the first place, that the atomic weights in question are the same as those of Berzelius. This will be seen from the following table:—

Names of the Elements.	Berzelian Atomic Weights.		Gerhardt's Atomic Weights.	New Atomic Weights.
	Referred to 100 of Oxygen.	Referred to 1 of Hydrogen.		
Hydrogen	6·25	1	1	1
Oxygen	100	16	16	16
Sulphur	201·16	32·2	32	32
Chlorine	221·3	35·5	35·5	35·5
Bromine	499·8	79·8	80	80
Iodine	792·99	126·8	127	127
Nitrogen.....	88·5	14·1	14	14
Phosphorus....	196	31·5	31	31
Arsenic	469·4	75·1	75	75
Carbon.....	75·12	12	12	12
Silicium	277·7	44·4, $\frac{2}{3}$ of which = 28	28	28
Tin	735·29	117·6	58·75	118
Barium	855·29	136·8	68	136·8
Strontium	545·9	87·3	43·8	87·3
Calcium	251·65	40·2	20	40
Magnesium....	158·14	25	12	24
Manganese	344·6	55·1	27·8	55·6
Iron.....	350·5	56·1	28	56
Zinc.....	406·59	65	32·5	65
Cadmium	696·77	111·4	55·7	111·4
Copper.....	395·6	63·3	31·5	63
Lead.....	1294·6	207	103·5	207
Mercury	1251·29	200·2	100	200
Silver	1351·6	215·6	108	108
Potassium	489·9	78·3	39	39
Sodium	290·9	46·5	23	23
Lithium	81·66	13	6·5	6·5

It will be seen that the atomic weights in the second column are, for a considerable number of metals, double of those proposed by Gerhardt. It is these double atomic weights that are represented by the barred symbols of the preceding formulæ, which, in fact, are

identical with the old formulæ of Berzelius:* for the bars, which are, perhaps, necessary during the existing confusion of symbols, are merely provisional and will ultimately fall into disuse.

These double atomic weights are applicable to the diatomic metals above-mentioned, but not to *silver, potassium, sodium,* and *lithium,* which are monatomic and comparable with hydrogen. With regard then to the metals included in the preceding table, we adopt the atomic weights of Berzelius, excepting for the last four metals, which retain the smaller atomic weights adopted by Gerhardt.

The new system of atomic weights accords better than any other, with the physical data which serve to control the determination of the relative weights of the atoms. In fact, the numbers in the last column are identical with those designated by M. Regnault as "thermic equivalents." This philosopher has observed that the law of Dulong and Petit, according to which, the specific heats of the elementary bodies are to one another in the inverse ratio of their atomic weights, presents but few exceptions; and that even these disappear if we admit for hydrogen, potassium, sodium, and silver equivalents half as great as those generally adopted,—that is to say, if, while we retain the usual equivalents of the other elements, we assign to the four bodies just mentioned, the numbers $\frac{1}{2}$, $\frac{39}{2}$, $\frac{23}{2}$, $\frac{108}{2}$. It is easy to see that the equivalents, or rather atomic weights, of this system are identical with those in the last column of the preceding table.

According to the recent experiments of M. Regnault, the specific heat of crystallized silicium forms an exception to the law of Dulong and Petit: but this exception may be attributed to a peculiar molecular constitution resulting from the allotropic states of this element: for the former experiments of M. Regnault have taught us, that among the several allotropic modifications of carbon, there is but one, viz., lamp-black, whose specific heat satisfies the law in question,—whereas those of diamond and graphite, the allotropic states of which are similar to those of silicium, deviate from that law.†

In the next place, the new system of atomic weights is in harmony with the law of isomorphism, which requires that

* Berzelius wrote BaO, BaS, $BaO.H_2O$, $BaCl_2$, $BaSO_4$, &c. We return to these formulæ, but we agree with Gerhardt in writing K_2O, K_2S, KHO, KCl, K_2SO_4, &c.

† See on this point, the important remarks of Mr. Brodie on the atomic weight of graphite. Phil. Trans. 1859, p. 249.

isomorphous bodies be represented by analogous formulæ. Thus cuprous sulphide, which is isomorphous with sulphide of silver, Ag_2S, is expressed in the new system by the formula Cu_2S, whereas Gerhardt assigned to it the formula Cu_4S. Again, the sulphates of silver and of sodium are represented by the analogous formulæ SAg_2O_4 and SNa_2O_4. The isomorphous sulphates of the magnesian series are expressed by the formula—

$$SMO_4 + 7H_2O.*$$

The composition of the double sulphates of the same series is respresented by the formula—

$$SMO_4 \,.\, SR_2O_4 + 6H_2O.$$

Lastly, the system of atomic weights which we adopt is in harmony with the vapour-densities of a very considerable number of bodies. The exceptions observed, relate to the vapour-densities of certain elementary bodies.† Thus the atomic weights of phos-

* A large number of salts contain quantities of water, which, in Gerhardt's notation, must be represented by a fractional number of molecules ($H_2O = 18$). Now this inconvenience is obviated if we double the atomic weights of a certain number of the metals, as may be seen by the following examples:—

Gerhardt's Notation.		New Notation.	
$NiCl$	$+ 4\frac{1}{2}\ H_2O$	$Ni''Cl_2$	$+ 9\ H_2O$
$\left.\begin{matrix}Cu\\NO_2\end{matrix}\right\}O$	$+ 1\frac{1}{2}\ H_2O$	$\left.\begin{matrix}Cu''\\2NO_2\end{matrix}\right\}O_2$	$+ 3\ H_2O$
$\left.\begin{matrix}Cu\\C_2H_3O\end{matrix}\right\}O$	$+ \frac{1}{2}\ H_2O$	$\left.\begin{matrix}Cu''\\2(C_2H_3O)\end{matrix}\right\}O_2$	$+ H_2O$
$\left.\begin{matrix}Pb\\C_2H_3O\end{matrix}\right\}O$	$+ 1\frac{1}{2}\ H_2O$	$\left.\begin{matrix}Pb''\\2(C_2H_3O)\end{matrix}\right\}O_2$	$+ 3\ H_2O$
$\left.\begin{matrix}Pb\\ClO_3\end{matrix}\right\}O$	$+ 1\frac{1}{2}\ H_2O$	$\left.\begin{matrix}Pb''\\2(ClO_3\end{matrix}\right\}O_2$	$+ 3\ H_2O$
(Roscoe)		(Roscoe)	

† The atomic weights of the elementary bodies (referred to 1 volume) are obtained by multiplying their vapour-densities by $14{\cdot}44 = \frac{1}{0.0693}$; and the molecular weights (referred to 2 volumes) are obtained by multiplying the vapour-densities by $28{\cdot}88 = \frac{2}{0.0693}$. But on multiplying the vapour-densities of mercury, 6·976, and of cadmium, 3·94, by 28·88, we find the numbers 201·4 and 113·7; and the anomaly exhibited by these metals may be expressed by saying, that their molecular weights, such as are deduced from their vapour-densities, really represent their atomic weights ($200 = Hg$; $111{\cdot}5 = Cd$). On the other hand, if we multiply the vapour-densities of phosphorus, 4·42, and of arsenic, 10·6, by 14·44, we obtain the numbers 63·8 and 153, an anomaly which may be expressed by saying, that the atomic weights of these bodies, as deduced from their vapour-densities, really express their molecular weights ($PP = 63$; $As\,As = 150$).

phorus, arsenic, mercury, zinc and cadmium, calculated from their vapour-densities, do not agree with those which are deduced from other considerations. These cases may, however, be regarded as exceptional, if we remember that the atomic weights of a large number of compounds into which these elements enter, are in accordance with the atomic weights in question. We will cite a few examples, confining ourselves to the diatomic and tetratomic metals :—

	Vapour-densities.	Molecular weights deduced from vapour-densities.	Molecular weights.	Formulæ.
Chloride of silicium .	5·939	171	170	$SiCl_4$
Chloride of zirconium	8·21	237		Zr_2Cl_4
Chloride of titanium .	6·836	197	190·2	$TiCl_4$
Stannic chloride . . .	9·2	265	260	$SnCl_4$
Stannethyl	8·021	232	234	$Sn(C_2H_5)_4$
Zinc-ethyl	4·259	123	124	$Zn(C_2H_5)_2$
Mercuric chloride . .	9·42	271	271	$HgCl_2$
Mercuric bromide . .	12·16	351	360	$HgBr_2$

If then we adopt for the metals in question, atomic weights twice as great as those usually assigned to them, and accordingly regard the metals as diatomic, we shall be able to compare oxide of ethylene with the oxides of these metals. This organic oxide thus becomes the analogue of baryta, just as oxide of ethyl is the analogue of oxide of silver, and oxide of glyceryl the analogue of oxide of antimony.

$$\left.\begin{matrix}Ag'\\Ag'\end{matrix}\right\}O \qquad Ba''O \qquad \left.\begin{matrix}Sb'''\\Sb'''\end{matrix}\right\}O_3$$

$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O \qquad C_2H_4O \qquad \left.\begin{matrix}C_3H_5\\C_3H_5\end{matrix}\right\}O_3.$$

I. We know that caustic baryta is capable of absorbing oxygen and passing to a higher degree of oxidation, viz., the bioxide of barium. Oxide of ethylene possesses the same property, although the reaction takes place under different conditions, and the pro-

duct, instead of being neutral, like bioxide of barium, exhibits the properties of an acid. When an aqueous solution of oxide of ethylene is placed in contact with platinum-black, the liquid rapidly becomes acid, in consequence of the formation of glycolic acid, which constitutes the product of the direct oxidation of oxide of ethylene. The glyoxylic acid of Dr. Debus may be regarded as a higher oxide of the same products, so that we may construct the following series:—

$\overline{C}_2H_4$ ..... ethylene.
$\overline{C}_2H_4\overline{O}$ ..... oxide of ethylene.
$\overline{C}_2H_4\overline{O}_2$ ..... glycolic acid.
$\overline{C}_2H_4\overline{O}_3$ ..... glyoxylic acid.

We are acquainted with other series of the same kind in organic chemistry, and these series, be it observed, have their analogues in mineral chemistry.

Laurent established the following series:*—

ClH	PH_3
$ClH\overline{O}$	$PH_3\overline{O}_2$
$ClH\overline{O}_2$	$PH_3\overline{O}_3$
$ClH\overline{O}_3$	$PH_3\overline{O}_4$
$ClH\overline{O}_4$	

and Odling developing this idea, has given other series of the same kind in his excellent "Manual of Chemistry."

II. Caustic baryta, to which we have just compared oxide of ethylene, unites directly with water to form hydrate of baryta. In like manner, oxide of ethylene is capable of fixing water, so as to form hydrate of oxide of ethylene, that is to say, glycol. Between the hydrates of organic chemistry and the hydrated oxides of mineral chemistry, we may establish the following parallel:—

$\left.\begin{matrix}K\\H\end{matrix}\right\}\overline{O}$	$\left.\begin{matrix}\overline{Ba}''\\H_2\end{matrix}\right\}\overline{O}_2$	$\left.\begin{matrix}Sb'''\\H_3\end{matrix}\right\}\overline{O}_3$	$\left.\begin{matrix}\overline{Ffe}^{vi}\ddagger\\H_6\end{matrix}\right\}\overline{O}_6$
Potassa.	Baryta.	Antimonic hydrate.	Ferric hydrate.
$\left.\begin{matrix}\overline{C}_2H_5\\H\end{matrix}\right\}\overline{O}$	$\left.\begin{matrix}(\overline{C}_2H_4)''\\H_2\end{matrix}\right\}\overline{O}_2$	$\left.\begin{matrix}(\overline{C}_3H_5)'''\\H_3\end{matrix}\right\}\overline{O}_3$	$\left.\begin{matrix}(\overline{C}_6H_8)^{vi}\\H_6\end{matrix}\right\}\overline{O}_6$
Alcohol.	Hydrate of ethylene. (glycol.)	Glycerin.	Hexylic hydrate (Mannite.)†

* Laurent's *Methode de Chemie*, translated by Odling, pp. 30, 31.
† Wanklyn and Erlenmeyer, Proceedings of the Royal Society, xi., 447.
‡ $\overline{Ffe} = Fe^4 = 112$.

But oxide of ethylene exhibits this remarkable peculiarity, that not only is *one* molecule of it capable of uniting with one molecule of water, but *two, three, four, five*, or more, molecules of oxide of ethylene can combine with a single molecule of water, to form hydrates belonging to more and more complex types. These hydrates constitute the polyethylenic alcohols, the first of which, viz., diethylenic alcohol, was discovered by M. Lourenço. They may be regarded as resulting from the partial dehydration of an increasing number of molecules of glycol.

$$2\left\{\begin{matrix}\mathrm{C_2H_4}\\ \mathrm{H_2}\end{matrix}\right\}\mathrm{O_2}\Big\} - \mathrm{H_2O} = \left.\begin{matrix}\mathrm{C_2H_4}\\ \mathrm{C_2H_4}\\ \mathrm{H_2}\end{matrix}\right\}\mathrm{O_3}$$

Glycol. Diethylenic alcohol.

$$3\left\{\begin{matrix}\mathrm{C_2H_4}\\ \mathrm{H_2}\end{matrix}\right\}\mathrm{O_2}\Big\} - 2\mathrm{H_2O} = \left.\begin{matrix}\mathrm{C_2H_4}\\ \mathrm{C_2H_4}\\ \mathrm{C_2H_4}\\ \mathrm{H_2}\end{matrix}\right\}\mathrm{O_4}$$

Triethylenic alcohol.

$$4\left\{\begin{matrix}\mathrm{C_2H_4}\\ \mathrm{H_2}\end{matrix}\right\}\mathrm{O_2}\Big\} - 3\mathrm{H_2O} = \left.\begin{matrix}\mathrm{C_2H_4}\\ \mathrm{C_2H_4}\\ \mathrm{C_2H_4}\\ \mathrm{C_2H_4}\\ \mathrm{H_2}\end{matrix}\right\}\mathrm{O_5}$$

Tetrethylenic alcohol.

The study of these bodies establishes a new property of ethylene, the power of accumulating in combination, and thereby forming compounds containing multiple radicles, and belonging to types of greater and greater complexity. This property is likewise possessed by other organic radicles. M. Friedel and myself have found it in acetyl, which accumulates in the polyacetic compounds, and M. Lourenço has observed it in glyceryl, which in like manner is capable of forming polyglyceric compounds. It is, therefore, a general property of polyatomic radicles, and ought to be found, not only in certain mineral groups, but likewise in the elements of mineral chemistry which are the representatives of these radicles.

Amongst mineral groups possessing the property in question, we may mention *sulphuryl, chromyl,* and *phosphoryl,* which may be supposed to exist in the following compounds :—

$$\left.\begin{matrix}\overline{S}O_2\\ \overline{S}O_2\\ H_2\end{matrix}\right\}O_3 \qquad \left.\begin{matrix}\overline{C}rO_2\\ \overline{C}rO_2\\ K_2\end{matrix}\right\}O_3 \qquad \left.\begin{matrix}(P\overline{O})'''\\ (P\overline{O})'''\\ H_4\end{matrix}\right\}O_5$$

Nordhausen sulphuric acid. Chromate of potassium. Pyrophosphoric acid.

Amongst elementary bodies which play the part of polyatomic radicles, we shall here consider only *tin* and *silicium* both tetratomic and capable of forming polystannic and polysilicic compounds.

1. *Stannic hydrate*, to which Mr. Graham has just called attention in his remarkable researches on dialysis, contains

$$\left.\begin{matrix}\overline{S}n^{iv}\\ H_4\end{matrix}\right\}O_4,$$

and yields, with loss of H_2O, a hydrate containing

$$\left.\begin{matrix}\overline{S}n^{iv}\\ H_2\end{matrix}\right\}O_3,$$

which is the stannic acid dried in vacuo, analysed by M. Fremy.

The composition of the *stannates* is represented by the formula

$$\left.\begin{matrix}\overline{S}n^{iv}\\ 2R'\end{matrix}\right\}O_3.$$

Metastannic hydrate, according to M. Fremy, contains within its molecule 5 atoms of tin, so that its composition is expressed by the formula

$$\left.\begin{matrix}5\overline{S}n^{iv}\\ H_{20}\end{matrix}\right\}O_{20}.$$

At 100°, it gives off half its water, and is converted into a hydrate,

$$\left.\begin{matrix}5\overline{S}n^{iv}\\ H_{10}\end{matrix}\right\}O_{15}.$$

The *metastannates* are represented by the formula

$$\left.\begin{matrix}5\overline{S}n^{iv}\\ H_8R_2\end{matrix}\right\}O_{15}.$$

We see then, that in metastannic hydrate and the metastannates, a number of atoms of tin are accumulated in one and the same molecule. The same property is exhibited by *silicium*, in various silicic hydrates and ethers, and in a very large number of silicates. This will be seen by a glance at the following

table, in which the formulæ ranged on the same horizontal line afford examples of continually increasing condensation, whilst those in the same vertical column represent the hydrates, or rather anhydrides, formed successively by the loss of a continually increasing number of molecules of water :—

$\left.\begin{matrix}\overset{\text{iv}}{Si}\\H_4\end{matrix}\right\}O_4$	$\left.\begin{matrix}Si\\Si\\H_8\end{matrix}\right\}O_8$	$\left.\begin{matrix}Si\\Si\\Si\\H_{12}\end{matrix}\right\}O_{12}$	$\left.\begin{matrix}Si_4\\H_{16}\end{matrix}\right\}O_{16}$	„	$\left.\begin{matrix}Si_6\\H_{24}\end{matrix}\right\}O_{24}$
$\left.\begin{matrix}Si\\H_2\end{matrix}\right\}O_3$	$\left.\begin{matrix}Si_2\\H_6\end{matrix}\right\}O_7$	$\left.\begin{matrix}Si_3\\H_{10}\end{matrix}\right\}O_{11}$	$\left.\begin{matrix}Si_4\\H_{14}\end{matrix}\right\}O_{15}$	„	„
	$\left.\begin{matrix}Si_2\\H_4\end{matrix}\right\}O_6$	$\left.\begin{matrix}Si_3\\H_8\end{matrix}\right\}O_{10}$	$\left.\begin{matrix}Si_4\\H_{12}\end{matrix}\right\}O_{14}$	„	„
	$\left.\begin{matrix}Si_2\\H_2\end{matrix}\right\}O_5$	$\left.\begin{matrix}Si_3\\H_6\end{matrix}\right\}O_9$	$\left.\begin{matrix}Si_4\\H_{10}\end{matrix}\right\}O_{13}$	„	„
		$\left.\begin{matrix}Si_3\\H_4\end{matrix}\right\}O_8$	$\left.\begin{matrix}Si_4\\H_8\end{matrix}\right\}O_{12}$	„	„
		$\left.\begin{matrix}Si_3\\H_2\end{matrix}\right\}O_7$	$\left.\begin{matrix}Si_4\\H_6\end{matrix}\right\}O_{11}$	„	$\left.\begin{matrix}Si_6\\H_8\end{matrix}\right\}O_{16}$

$\left.\begin{matrix}Si\\(C_2H_5)_4\end{matrix}\right\}O_4$	$\left.\begin{matrix}Si_2\\Ca''\\H_4\end{matrix}\right\}O_7$	$\left.\begin{matrix}Si_3\\All^{\text{vi}}\\2M'\end{matrix}\right\}O_{10}$*	$\left.\begin{matrix}Si_4\\All^{\text{vi}}\\2M'\end{matrix}\right\}O_{12}$	„	$\left.\begin{matrix}Si_6\\All^{\text{vi}}\\K_2\end{matrix}\right\}O_{16}$
Normal silicic ether.	Okenite.	Ryacolite.	Leucite.		Felspar (orthoclase.)

$\left.\begin{matrix}Si\\2Mg''\end{matrix}\right\}O_4$ $\left.\begin{matrix}Si\\Ca''\\Mg''\end{matrix}\right\}O_6$

Olivine. Diopside.

$\left.\begin{matrix}Si\\C(_2H_5)_2\end{matrix}\right\}O_3$ $\left.\begin{matrix}Si_2\\(C_2H_5)_2\end{matrix}\right\}O_5$

Diethylic silicate. Diethlyic disilicate.

We see then that this theory enables us to conceive, and even to predict, the existence of a very large number of silicates, and that it is not without reason that these compounds have received the

* All = Al^4 = 54·8

epithet *polysilicic*. Their constitution, and the formulæ which represent them, are not always very simple, and cannot be so in a great number of cases; but that which is really simple and rational is their mode of generation, based on the principle of the *accumulation of polyatomic radicles*. This principle, which likewise regulates the congregation of organic molecules, appears to be capable of a great number of applications in mineral chemistry, and is on this account well worthy of attention. We may also notice the part played, in the formation of these compounds, by the successive dehydration, of which hydrates containing polyatomic radicles are susceptible.

III. Oxide of ethylene unites directly with acids, forming salts which constitute the ethylenic ethers, or ethers of glycol. These reactions sometimes take place with great energy. Thus when oxide of ethylene is placed in contact with sulphuric acid, combination takes place, attended with a hissing noise and great evolution of heat. By operating with caution, and using an acid diluted with water, a nearly neutral liquid may be obtained, which remains in the syrupy state when evaporated. The combination of oxide of ethylene with acetic acid, also takes place at ordinary temperatures, producing monacetic or diacetic glycol, according as one or two molecules of acid enter into the reaction :—

$$\mathrm{C_2H_4O} + \left.\begin{matrix}\mathrm{C_2H_3O}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O} = \left.\begin{matrix}\mathrm{C_2H_4}\\ (\mathrm{C_2H_3O})\\ \mathrm{H}\end{matrix}\right\}\mathrm{O_2}$$

$$\mathrm{C_2H_4O} + 2\left\{\begin{matrix}\mathrm{C_2H_3O}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O} = \left.\begin{matrix}\mathrm{C_2H_4}\\ (\mathrm{C_2H_3O})_2\end{matrix}\right\}\mathrm{O_2} + \mathrm{H_2O}$$

Diacetic glycol may be formed directly by heating acetic anhydride with oxide of ethylene :—

$$\mathrm{C_2H_4O} + \left.\begin{matrix}\mathrm{C_2H_3O}\\ \mathrm{C_2H_3O}\end{matrix}\right\}\mathrm{O} = \left.\begin{matrix}\mathrm{C_2H_4}\\ (\mathrm{C_2H_3O})_2\end{matrix}\right\}\mathrm{O_2}.$$

Under these circumstances, then, oxide of ethylene behaves like a metallic oxide, and may be compared in this respect with oxide of copper or oxide of lead. When a single molecule of acetic acid acts upon oxide of lead, the so-called *bibasic acetate of lead* is formed, which may be compared with monoacetate of ethylene :—

$$\left.\begin{matrix}(C_2H_4)''\\ C_2H_3O\\ H\end{matrix}\right\}O_2 \qquad \left.\begin{matrix}Pb''\\ C_2H_3O\\ H\end{matrix}\right\}O_2 + H_2O$$

Monoacetate of ethylene. (so-called) Bibasic acetate of lead.

But when two molecules of acetic acid act upon a molecule of oxide of copper or oxide of lead, *neutral acetates* are formed comparable with ethylenic diacetate:—

$$\left.\begin{matrix}(C_2H_4)''\\ (C_2H_3O)_2\end{matrix}\right\}O_2; \quad \left.\begin{matrix}Cu''\\ (C_2H_3O)_2\end{matrix}\right\}O_2 + H_2O; \quad \left.\begin{matrix}Pb''\\ (C_2H_3O)_2\end{matrix}\right\}O_2 + 3H_2O$$

Ethylene diacetate. Diacetate of copper (Cristaux de Venus). Diacetate of lead (Sal Saturni; sugar of lead)

But the analogy of all these reactions may be drawn still closer; for, just as several molecules of oxide of copper or oxide of lead can unite with acetic acid, so likewise may two, three, four, or more molecules of oxide of ethylene combine with acetic acid to form polyethylenic acetates. A glance at the following formulæ will be sufficient to show the analogy between the basic salts formed by certain mineral oxides, and these polyethylenic acetates:—

$$\left.\begin{matrix}(C_2H_4)''\\ (C_2H_4)''\\ (C_2H_3O)_2\end{matrix}\right\}O_3 \qquad \left.\begin{matrix}Cu''\\ Cu''\\ (C_2H_3O)_2\end{matrix}\right\}O_3 + 3H_2O \qquad \left.\begin{matrix}Pb''\\ Pb''\\ NO\\ NO_2\end{matrix}\right\}O_3$$

Diethylenic acetate. Dicupricacetate. Nitroso-nitrate of lead (Peligot's bibasic hyponitrate of lead).

$$\left.\begin{matrix}(C_2H_4)_3''\\ (C_2H_3O)_2\end{matrix}\right\}O_4 \qquad \left.\begin{matrix}Cu_3''\\ (C_2H_3O)_2\end{matrix}\right\}O_4 \qquad \left.\begin{matrix}Pb_3''\\ (C_2H_3O)_2\end{matrix}\right\}O_4 + 3H_2O$$

Triethylenic acetate. Tricupric acetate (heated to 160°). Triplumbic acetate.

These basic salts owe their existence and formation to the tendency possessed by polyatomic radicles, both simple and compound, of accumulating in combinations. We are not acquainted with any well-defined basic salts formed by the union of monobasic acids with the oxides of potassium, sodium, lithium, and silver; and the power of forming basic salts, possessed by most other oxides, may, perhaps, be altogether dependent on the polyatomic nature of their metallic radicles. The following facts, however, exhibit this polyatomicity in a still clearer light:—

Oxide of ethylene possesses the power of uniting with two different monobasic acids. We are, in fact, acquainted with ethylenic ethers containing two different acid-radicles, such compounds having been obtained by Dr. Maxwell Simpson and M. Lourenço. In like manner there exist metallic salts produced by the reaction of two different monobasic acids on a diatomic oxide or hydrate. From this point of view, we may compare aceto-butyric glycol with nitro-acetate of strontium or baryta:—

$$\left.\begin{matrix}(C_2H_4)''\\H_2\end{matrix}\right\}O_2 \qquad \left.\begin{matrix}Sr''\\H_2\end{matrix}\right\}O_2 \qquad \left.\begin{matrix}Ba''\\H_2\end{matrix}\right\}O_2*$$

$$\left.\begin{matrix}(C_2H_4)''\\C_2H_3O\\C_4H_7O\end{matrix}\right\}O_2 \qquad \left.\begin{matrix}Sr''\\C_2H_3O\\NO_2\end{matrix}\right\}O_2 \qquad \left.\begin{matrix}Ba''\\C_2H_3O\\NO_2\end{matrix}\right\}O_2$$

In these compounds, the diatomic radicles, ethylene and strontium, perform exactly the same function as the diatomic radicle of tartaric acid in Rochelle salt, and the existence of the aceto-nitrate of strontium affords as strong an argument in favour of the double atomic weight of strontium, as that which was deduced by Liebig, from the existence of Rochelle salt, for doubling the formula of tartaric acid.

IV. Oxide of ethylene unites directly with chlorhydric acid. On mixing the two gases in equal volumes over mercury, they instantly disappear, just as ammonia gas disappears on being mixed with chlorhydric acid. The result of the combination is chlorhydrate of oxide of ethylene or chlorhydric glycol :—

$$\left.\begin{matrix}C_2H_4\\H_2\end{matrix}\right\}O_2 \qquad \left.\begin{matrix}C_2H_4\\H\\Cl\end{matrix}\right\}O \qquad \text{or} \qquad C_2H_4O.HCl$$

Glycol. Mono-chlorhydric glycol. Chlorhydrate of oxide of ethylene.

Is there in mineral chemistry any compound analogous to monochlorhydric glycol? I am not acquainted with any well defined metallic monochlorhydrin, but a sulphuric monochlorhydrin was discovered a few years ago by Professor Williamson:—

$$\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2 \qquad \left.\begin{matrix}SO_2\\H\\Cl\end{matrix}\right\}O_2$$

Sulphuric acid. Sulphuric monochlorhydrin.

* C. v. Hauer, J. pr. Chem. lxxiv, 431.

On the other hand, several well defined fluorhydrins are known, viz., oxyfluorides, or fluorides of oxides. Thus Berzelius analysed a well crystallised oxyfluoride of copper, and expressed its composition by the formula, CuFl.CuO.HO, which if we adopt the double atomic weights of oxygen and copper, becomes

$$\text{Cu''O} \,.\, \text{HFl}$$

Fluorhydrate of cupric oxide.

It is easy to see that this compound is related to cupric hydrate in the same manner as monochlorhydric glycol to glycol :—

$$\left.\begin{matrix}\text{Cu''}\\ \text{H}_2\end{matrix}\right\}\text{O}_2 \qquad\qquad \left.\begin{matrix}\text{Cu''}\\ \text{H}\\ \text{Fl.}\end{matrix}\right\}\text{O}$$

Cupric hydrate. Cupric monofluorhydrin.

There exist condensed chlorhydrins corresponding to the polyethylenic alcohols. Diethylenic alcohol is capable of forming two chlorhydrins, whose composition is represented by the following formulæ :—

$$\left.\begin{matrix}\text{C}_2\text{H}_4\\ \text{C}_2\text{H}_4\\ \text{H}_2\end{matrix}\right\}\text{O}_3 \qquad \left.\begin{matrix}\text{C}_2\text{H}_4\\ \text{C}_2\text{H}_4\\ \text{H}\\ \text{Cl}\end{matrix}\right\}\text{O}_2 \qquad \left.\begin{matrix}\text{C}_2\text{H}_4\\ \text{C}_2\text{H}_4\\ \text{Cl}_2\end{matrix}\right\}\text{O}$$

Diethylenic alcohol. Monochlorhydrin of diethylenic alcohol. Dichlorhydrin of diethylenic alcohol.

The monochlorhydrin of diethylenic alcohol is obtained by heating chlorhydric glycol with oxide of ethylene :—

$$\text{C}_2\text{H}_5\text{ClO} + \text{C}_2\text{H}_4\text{O} = \left.\begin{matrix}\text{C}_2\text{H}_4\\ \text{C}_2\text{H}_4\\ \text{H}\\ \text{Cl}\end{matrix}\right\}\text{O}_2 \;=\; \text{HCl}.(\text{C}_2\text{H}_4)_2\text{O}_2.$$

It is a liquid boiling at about 180°. The dibromhydrin of diethylenic alcohol is probably formed when oxide of ethylene is boiled for a long time with bromide of ethylene (unpublished experiments) :—

$$\text{C}_2\text{H}_4\text{Br}_2 + \text{C}_2\text{H}_4\text{O} = \left.\begin{matrix}\text{C}_2\text{H}_4\\ \text{C}_2\text{H}_4\\ \text{Br}_2\end{matrix}\right\}\text{O}_2.$$

This last compound may be compared with the bromides and chlorides of mineral oxides. It will be interesting to establish this analogy by a few examples.

Hydrate of lime dissolves in a solution of chloride of calcium, and the alkaline liquid, when concentrated, yields on cooling hydrated crystals, to which H. Rose assigns the formula $3CaO.CaCl + 16HO$. In our notation, this formula becomes $3\overline{C}a\overline{O}.\overline{C}aCl_2 + 16H_2\overline{O}$, and may be written as follows:—

$$\left.\begin{matrix}\overline{C}a\\ \overline{C}a\\ \overline{C}a\\ \overline{C}a\end{matrix}\right\}O_3 + 16H_2\overline{O}, \text{ which is analogous to } \left.\begin{matrix}\overline{C}_2H_4\\ \overline{C}_2H_4\\ \overline{C}_2H_4\\ \overline{C}_2H_4\end{matrix}\right\}\overline{O}_3$$
$$Cl_2 \qquad\qquad Cl_2$$

Dichlorhydrin of tetrethylenic alcohol.

There are also oxychlorides of lead possessing an analogous constitution. Thus *Mendipite*, which is a well crystallised mineral, contains

$$2\overline{P}bO.\overline{P}bCl_2 = \overset{\overline{P}b_3\overline{O}_2}{Cl_2}.$$

Atacamite is a hydrated oxychloride of copper composed of

$$3\overline{C}uO.\overline{C}uCl_2 = \overset{\overline{C}u_4\overline{O}_3}{Cl_2}.$$

Other facts belonging to mineral chemistry may likewise be compared with the preceding. Thus the compounds formed when ferric oxide is dissolved in a solution of ferric chloride (and we know that it dissolves abundantly) are doubtless analogous to the chlorhydrins. On the other hand, H. Rose has shewn that the solution, obtained by treating stannic chloride with water, possesses characters totally different from those which are exhibited by the chlorhydric solution of metastannic acid.* From the molecular constitution of this acid, we may suppose that its chlorhydric solution contains a polystannic chlorhydrin.

V. Dr. Maxwell Simpson has described, under the name of glycolic chloraceten (aceto-chlorhydric glycol) a mixed ether of glycol, which he has obtained by subjecting that body to the simultaneous† action of acetic and chlorhydric acids. This com-

* Pogg. Ann. cv. 564.

† Proceedings of the Royal Society, ix, 725.

pound contains $\left.\begin{matrix}(\overline{C}_2H_4)'' \\ (\overline{C}_2H_3\overline{O})'\end{matrix}\right\}\overline{O}$; or, as it may be more simply written, $\left.\begin{matrix}(\overline{C}_2H_4)'' \\ (\overline{C}_2H_3\overline{O})'\end{matrix}\right\}\begin{matrix}\overline{O} \\ Cl.\end{matrix}$

We are acquainted with certain mineral compounds of analogous constitution, excepting that in place of acetyl, they contain polybasic acid radicles. Thus *Wagnerite* and *Apatite*, which are well characterised mineral species, are fluophosphates of magnesium and calcium, to which we may assign the formulæ

$$PO_5.3MgO + MgFl \text{ and } 3(PO_5.3CaO) + CaFl,$$

which in our notation become

$\left.\begin{matrix}(P\overline{O})''' \\ 2\overline{Mg}''\end{matrix}\right\}\begin{matrix}\overline{O}_3 \\ Fl\end{matrix}$ and $\left.\begin{matrix}3(PO)''' \\ 5\overline{Ca}''\end{matrix}\right\}\begin{matrix}\overline{O}_9 \\ Fl\end{matrix}$

Wagnerite. Apatite.

Wagnerite and Apatite are in fact the phosphofluorhydrins of the hydrates

$\left.\begin{matrix}(P\overline{O})''' \\ H_5\end{matrix}\right\}\overline{O}_4$ and $\left.\begin{matrix}(P\overline{O})_3''' \\ H_{11}\end{matrix}\right\}\overline{O}_{10}$.

And here we have occasion for an important remark. Ordinary phosphoric $\left.\begin{matrix}(P\overline{O})''' \\ H_3\end{matrix}\right\}\overline{O}_3$ requires to saturate it more than one atom of magnesium ($\overline{Mg}'' = 24$), but two atoms of this magnesium, which are equivalent to four atoms of hydrogen, are too much for the purpose. Now, Wagnerite contains exactly two atoms of magnesium; it would therefore be supersaturated if the fourth combining unit of the group $2\overline{Mg}''$ were not saturated by the fluorine. The same reasoning applies to apatite and to the calcium contained in it. We see, therefore, that in these compounds, whose constitution appears so strange when regarded from the dualistic point of view, the fluorine or the chlorine plays an important and necessary part. I may add, that the presence of such a monatomic element in these compounds furnishes an argument in favour of the diatomicity of magnesium and of calcium. If magnesium were monatomic, the fluorine would be useless; for 3Mg [Mg = 12] could replace 3H in ordinary phosphoric acid. But the magnesium or the calcium being diatomic, and therefore

of even atomicity, the presence of a monatomic element becomes necessary to fill up the uneven atomicity of the phosphoryl $(P\overline{O})'''$.*

Other compounds may likewise be regarded from this point of view. There exists a chlorophosphate of lead exactly analogous in constitution to apatite, and we know that the phosphoric acid in this chlorophosphate may be replaced by arsenic acid.

Gerhardt has analysed a mercurous nitrophosphate which contains a molecule of mercurous phosphate united with a molecule of mercurous nitrate. This compound, represented by the formula $Hg_2O.NO_5 + 3Hg_2O.PO_5 + 2HO$ may be considered a kind of Wagnerite, in which the magnesium is replaced by mercurosum [$\overline{Hg}_2 = 400$], and the fluorine by nitrous vapour:—

$$2\left[\begin{matrix}(P\overline{O})'''\\ \overline{Hg}_2\end{matrix}\right]''\Bigg\}\ \overline{O}_3 \quad (N\overline{O}_2)' \quad + \quad H_2\overline{O}.$$

VI. Just as the diatomic radicle, ethylene can join together two molecules of water, when it takes the place of two atoms of hydrogen to form glycol, so likewise is it capable of uniting two molecules of ammonia to form ethylene-diamine. I do not intend to give in this place a general view of the ethylenic polyamines—for our knowledge of which we are indebted to the classic researches and rare sagacity of Dr. Hofmann—but merely to call attention to the analogy existing between these compounds and certain mineral polyamines.

Diatomic metals are capable of replacing ethylene in the diamines. Compounds of this kind are known, and rational formulæ, for expressing the constitution of various metallic polyamines,

* My friend Dr. Odling has called my attention to a salt described by Briegleb (Ann. Ch. Pharm. xcviii. 95), and represented by the formula $3NaO.PO_5 + NaFl + 24HO$. Without attempting to deny that the existence of this salt may weaken the argument afforded by the constitution of Wagnerite in favour of the diatomicity of magnesium, I will nevertheless observe: 1. That the salt is very unstable, being resolved, by boiling, into phosphate and fluoride. 2. That it has not been found possible to form a corresponding salt of potassium. 3. That this salt is not strictly comparable with Wagnerite, inasmuch as it contains water of crystallisation.

We are indebted to M. Cannizzaro for another chemical argument in favour of the diatomicity of calcium and barium—namely, that whereas there exists a quadroxalate of potassium, we are not acquainted with a quadroxalate of calcium or of barium. In fact, a single atom of hydrogen in two molecules of oxalic acid may be replaced by an atom of potassium, but not by an atom of diatomic calcium, which is equivalent to two atoms of hydrogen. If then a portion of the hydrogen in two molecules of oxalic acid is replaced by calcium or barium, the result of the substitution can only be a bioxalate.

have lately been proposed by MM. Weltzien and Hugo Schiff. I shall consider in this place only the formulæ given by Schiff for the cupric amines, viz. :—

$$N\begin{cases}Cu\\H\\H\\H\end{cases} \qquad \text{and} \qquad N\begin{cases}Cu\\Am\\H\\H\end{cases}$$

Cupriconium. Amicupriconium.

I double these formulæ, and suppose that in the cupric diamines, the diatomic radicle, copper, joins together two molecules of ammonium, just as ethylene does in ethylenic diammonium. I therefore write the formulæ of the cupric diammoniums as follows :—

$$N_2\begin{cases}(\overline{C}_2H_4)''\\H_2\\H_2\\H_2\end{cases} \quad N_2\begin{cases}\overline{C}u''\\H_2\\H_2\\H_2\end{cases} \quad N_2\begin{cases}\overline{C}u''\\Am_2\\H_2\\H_2\end{cases} \quad N_2\begin{cases}\overline{C}u''\\Am_2\\Am_2\\H_2\end{cases}$$

Ethylene-diammonium. Cupriconium. Diamicupriconium. Tetramicupriconium.

$$\left[N_2\begin{cases}\overline{C}u''\\H_6\\(\overline{C}_2H_3\overline{O})_2\end{cases}\right]'' \Big\} \overline{O}_2 + 2H^2\overline{O} \qquad \left[N_2\begin{cases}\overline{C}u''\\Am_4\\H_2\\(S\overline{O}_2)''\end{cases}\right]'' \Big\} \overline{O}_2 + 2H\overline{O}_2$$

Acetate of cupriconium. Sulphate of Tetramicupriconium (ammonio-sulphate of copper).

Besides the ethylene-bases, we are acquainted with another class of bases, called *oxyethylenic*. They are formed by the direct combination of oxide of ethylene with ammonia. One, two, three, four molecules of oxide of ethylene can unite with a single molecule of ammonia to form bases of greater and greater complexity, and this combination takes place at ordinary temperatures, energetically and without elimination of water : so great is the combining power of oxide of ethylene. It appears to me—and with this consideration I will conclude—that there exist in mineral chemistry bases analogous to the oxyethylenic bases. M. Millon discovered, some years ago, a remarkable base, to which he gave the name of *ammonio-mercuric oxide*. It is formed by the action of ammonia on mercuric oxide. Its composition is usually represented by the formula $3HgO.HgH_2N + 3HO$, which, trans-

lated into our notation, independently of any hypothesis respecting the molecular arrangement, becomes—

$$2\overline{Hg}\overline{O}.NH_3 + H_2\overline{O};$$

according to which, ammonio-mercuric oxide would be the analogue of *dioxethylenamine*—

$$2(\overline{C}_2H_4\overline{O}).NH_3.$$

According to the experiments of M. Millon, this base can give off more than one molecule of water in drying, and, when perfectly dry, contains $3HgO.HgN_2H_2$, or, in our notation, $3\overline{Hg}\overline{O}.\overline{Hg}N_2H_4$. Here again we may perceive a certain analogy between these facts and those which are observed in organic chemistry; we know indeed that the oxyethylenic bases are converted, by loss of water, into vinylic bases.

Such are the considerations which I have ventured to put forward on the analogies existing between organic and mineral compounds. I have endeavoured to follow out these analogies in the most various classes of bodies, and to express them in the typical notation, so well adapted to comparisons of this nature. I shall think myself happy if I have succeeded in impressing more forcibly on the minds of my auditors this truth, which everybody is ready to enunciate, but which few have undertaken to establish by strict demonstration—namely, that *there is but one Chemistry, and that the laws which regulate the constitution of Organic bodies apply with equal force to the compounds of Mineral Chemistry and Mineralogy.*

XLIX.—*On the Chemistry of Digestion.*

[A Discourse delivered to the Fellows of the Chemical Society.]

By W. Marcet, M.D., F.R.S.,

Assistant Physician to the Westminster Hospital, etc.

By the chemical phenomena of digestion, we mean those chemical changes which food undergoes in the stomach and intestines, the object of which is to transform it into certain soluble substances on the one hand, and into emulsions on the other; for under those conditions only, can the food taken be absorbed into the blood-vessels and lacteals, and thereby effect the purpose of nutrition. If from some circumstance connected with the nature of the ingesta, or a vitiated state of the gastric and intestinal secretions, the metamorphosis in question does not take place, what has been eaten will be voided, more or less unaltered,—a fact of importance in a medical point of view.

My attention has been directed for many years to the subject of the present discourse, and I avail myself, with pleasure, of this opportunity of recording the valuable aid of my former assistant, Dr. Frederick Dupré, in a considerable portion of these inquiries.

The stomach, during the period of fasting, contains a small quantity of mucus, exhibiting a slight, though decided, alkaline reaction; this can be easily ascertained by testing the few drops of the ropy and frothy fluid obtained from the stomach of a dog having a gastric fistula, or external opening in that organ. As soon as solid food is taken, the stomach secretes in abundance a strongly acid fluid, the gastric juice, and the process of digestion commences. The action of the gastric juice on the contents of the stomach is generally considered as due to its acid constituent, and to a substance called *pepsin*, which it contains in very small quantity. It should be remembered, however, that every one of the constituents of gastric juice must have a share in its action on food; just in the same way as certain therapeutical agents, such as mineral waters, are possessed of medicinal properties, partly on account of a special substance they contain, and partly from the united influence of the whole of their constituents. Owing to this circumstance,

it is important when experimenting on gastric juice, to use, as far as possible, the secretion obtained from an animal, such as the dog, and avoid conducting the inquiry with a digestive fluid prepared artificially by mixing together a dilute acid and pepsin. I invariably used in my researches the gastric juice of four dogs, extracted from each animal through a gastric fistula with which it had been provided. The secretion was excited with hard-boiled cartilage, or soft bones. By this means I obtained, from two dogs, about a gallon of gastric juice; and a much larger amount could have been extracted within the same time, had it been required.

In order to determine the composition of pure gastric juice, it would be necessary to excite its secretion by means of hard substances, perfectly insoluble in that fluid: unfortunately, under those circumstances, as for instance, when dogs are made to swallow pebbles, the quantity of gastric juice secreted is but very small, and barely sufficient for a chemical inquiry. It must be remembered that hard animal tissues, such as cartilage, or even bone, are rapidly acted upon by gastric juice, so much so, that the fluid obtained from the stomach after the ingestion of these substances cannot be regarded as the pure secretion.

The acidity of gastric juice may be considered as one of its characteristic features. It is remarkable that chemists and physiologists do not yet agree as to the nature of this free acid, although, from the investigations of Bidder and Schmidt, Dr. Prout's opinion on the subject now prevails, and the acid substance is believed to be hydrochloric acid; the experiment which Bidder and Schmidt undertook in order to resolve the question, was as follows:—

"About 100 grammes of gastric juice were used, to which nitric acid and nitrate of silver were added; the amount of chloride of silver obtained was determined, which yielded the weight of the whole of the hydrochloric acid present. After the excess of nitrate of silver had been removed from the gastric juice by precipitation with hydrochloric acid, the fluid was evaporated to dryness, carefully incinerated, and the weight of the bases determined; the quantity of hydrochloric acid necessary to neutralize these bases was then calculated." By so doing, Messrs. Bidder and Schmidt obtained, on the one hand, the weight of the whole of the hydrochloric present in gastric juice, and on the other, the weight of the hydrochloric acid necessary to neutralize the bases; and as they found that the total amount of hydrochloric acid present was

greater than was necessary to neutralize the bases, they concluded that gastric juice contained some free hydrochloric acid. In order to decide whether there was any free acid in gastric juice besides hydrochloric acid, these enquirers determined the acidity of gastric juice with an alkaline normal solution, and they found the amount of the base necessary for the neutralization of this free acid to be exactly, or nearly equivalent to the quantity of free hydrochloric present, which had been ascertained in the first part of the experiment; they therefore concluded that the whole of the free acid of gastric juice is hydrochloric acid.

Notwithstanding the apparent correctness of this method of investigation, the gastric juice of a dog on which I have experimented, has appeared to me, for the following reason, to contain more or less of another acid besides hydrochloric acid. I happened to place some gastric juice in Graham's dialyser, which was made to float on distilled water. After a time, the secretion contained in the dialyser had lost certain of its immediate principles, which had passed into the distilled water. At first the acid gastric juice gave an abundant precipitate with nitrate of silver, but the bulk of the precipitate gradually diminished, the hydrochloric acid passing into the distilled water; and, finally, after coagulating the albumin by heat, and filtering, the addition of the reagent failed to give even a trace of a precipitate, thereby showing that the hydrochloric acid had entirely found its way through the membrane. On testing the fluid in the dialyser at that period of the experiment, it exhibited a distinctly acid reaction; consequently the gastric juice was still acid, although it did not contain a trace of hydrochloric acid, showing that another acid was present besides the hydrochloric acid.

The acidity of gastric juice, according to Bidder and Schmidt, ranges from 0·1708 to 0·3353 % of hydrochloric acid. I have had frequent opportunities of testing the degree of acidity of this secretion, and have found it to correspond to between 0·085 and 0·303 % of hydrochloric acid; these numbers, being rather lower than those of Bidder and Schmidt. While enquiring into the acidity of gastric juice, I observed that the degree of this re-action varied according to the period after the ingestion of food, at which the fluid was collected. The first quantity removed from the stomach was the most abundant, but the least acid; gradually less and less of the secretion could be obtained, but it became more and more acid; while the last quantities

of the gastric juice which were extracted exhibited the maximum degree of acidity. The following is a table showing the quantities of gastric juice extracted from a dog bearing a gastric fistula, at different periods after the animal was fed, and also the degree of acidity of the fluid, expressed as potash, necessary to neutralize 100 CC. of the secretion. In four experiments the acidity invariably increased, so much so that the degree of acidity was considerably greater towards the close of each experiment than it was at the beginning.

Acidity of Gastric Juice.

The *time* is counted just after the dog took his meal, consisting of boiled wind-pipe. The *acidity* is expressed in grammes of potash necessary to neutralize 100 CC. of gastric juice. The experiments were made in middle of March, 1860.

Time after food taken.	Quantity.	Acidity.
	No. I.	
30 minutes	2oz.	0·065
40^{m} later	1oz.	0·113
	No. II.	
30 minutes	lost.	
30^{m} later	2oz. 2dr.	0·130
10^{m} later	7dr.	0·156
10^{m} later	6dr.	0·169
10^{m} later	5dr.	0·195
	No. III.	
30 minutes	7dr.	0·208
30^{m} later ...	1oz. 6dr.	0·227
30^{m} later	1oz.	0·273
30^{m} later	3dr.	0·377
30^{m} later ...	1oz. 5dr.	0·390
	No. IV.	
39 minutes	2oz. 6dr.	0·180
10^{m} later	1oz. 3dr.	0·190
17^{m} later	2oz. ½dr.	0·235
15^{m} later	1oz. 4dr.	0·250
8^{m} later	5dr.	not determined.

This gradual increase of the acidity of gastric juice must be due, partly to the first quantities which are secreted being diluted and neutralized by the slightly alkaline mucus contained in the fasting stomach; but more especially, I believe, because the fluid secreted towards the end of digestion, is really more acid than that secreted at the beginning. This last hypothesis appears probable, if it be remembered that the mucus of the stomach, during the period of fasting, is but slightly alkaline, and exists therein but in small quantity. Whatever be the cause of the fact, the gradually increasing acidity of gastric juice, after food has been taken, appears established, and must serve some important purpose in connection with the process of digestion, one of these objects being obviously to add to the power of the stomach of digesting those pieces of food which have not been properly masticated. The outside of each morsel of animal food, which has been masticated, will not require for its digestion the action of strong gastric juice; but the inside of the morsel, especially in the case of animals, which is not so well triturated with the teeth, will require for its digestion the action of a more powerful or more acid gastric juice.

If we consider the average acidity of gastric juice to be due to the presence of 0·253 % of hydrochloric acid; and, if it be admitted, with Bidder and Schmidt, that an adult man, weighing about ten stone, secretes in twenty-four hours about 6400 grammes of gastric juice, then no less than about sixteen grammes (247 grns.) of free hydrochloric acid will be extracted from a human adult's blood, and returned into it in twenty-four hours. This acid must result from the decomposition of chloride of sodium, as was suggested by Prout* in 1834; but he adds "What becomes of the soda from which the muriatic acid has been disunited?" He proceeds to state, as his belief, that the largest part of this soda is probably directed to the liver, and passes off in the bile. We are now aware that such is not the case, and Dr. Bence Jones, by his researches on the acidity of the urine during the period of digestion and fasting, has solved this interesting question.† Blood is always alkaline; it must be so for the maintenance of health.‡ There is, however, in the blood a constant tendency to the forma-

* Chemistry, &c., of Digestion, 1834, p. 500. † Phil. Trans. 1849.

‡ Dr. Pavy has observed that, after phosphoric acid has been injected into the circulation, the urinary secretion contains sugar.

tion of acid; but, before the blood can turn acid, the excess of this substance is eliminated by the secretions; consequently acids are constantly being secreted from the blood, sometimes in the perspiration, sometimes in the urine, sometimes by the stomach. When the secretion of acid in the urine is active, that of the stomach is quiescent, and *vice versâ;* during the secretion of gastric juice, the acidity of the urine is greatly diminished. At the time when digestion is at its height, the acidity of the urine is at its minimum. These are the interesting results of Dr. Bence Jones' inquiries. We may therefore surmise that, during digestion, the chloride of sodium of the blood yields hydrochloric acid to the gastric juice, while the soda is immediately taken up by the acid, which, during fasting would have been excreted with the urine, but which remains in the circulation while digestion is going on.

If chloride of sodium be the source of the principal constituent of the gastric juice—*hydrochloric acid*—this salt must be one of the most important immediate principles of the blood; and we can understand, why, when animals are for a time comparatively deprived of chloride of sodium in their food, they eliminate none of this salt in their excrementitious secretions; and, consequently, in such cases, the same hydrochloric acid serves over and over again for the gastric secretion, while all the other constituents of the body are undergoing the normal process of waste. This is one of those admirable provisions of nature which have fitted animal life to be preserved under so many different circumstances.

The main object of the gastric digestion is the transformation of albuminous food into a substance which Lehmann has called *peptone,* and the conversion of neutral fats into fatty acids. Albumin, fibrin, casein, gelatin, and chondrin are modified in the stomach, and assume new characters, obviously in great measure with a view to their more ready absorption into the blood. Under the influence of the gastric juice, albuminous or protein-compounds lose their coagulability by heat and mineral acids, and likewise their property of forming insoluble combinations with most metallic salts. Lehmann has been unable to discover any difference between the quantities of nitrogen, carbon, oxygen, and sulphur contained in the peptone and in the substance from which it was derived. As to cartilage and gelatigenous bodies, they are converted in the stomach into substances which, according to Lehmann, correspond perfectly in their physical, and in most of their chemical properties to the peptones of the protein-bodies. We

gather from the observations of this chemist, that, in his opinion, the various peptones derived from protein and gelatin compounds are sufficiently analogous to be considered as one and the same body. Peptones must be looked upon as modifications of albumin, fibrin, casein, gelatin, and chondrin, approximating to albumin of blood; indeed they are partly assimulated compounds.

Although I have no reason whatever to disbelieve Lehmann's views regarding the analogy existing between the chemical characters of peptones, still they do not appear to agree altogether in their physical properties; and this point is one of much interest. Some peptones, or perhaps only one kind of peptone, acts on polarised light, rotating the plane of polarisation to the left, while others appear to exhibit no such property.

I observed, in the spring of 1860, that gastric juice acts on polarised light; and for the following twelve months I diligently inquired into the various circumstances connected with this phenomenon. Shortly after my results had been communicated to this Society, I found in Henle and Meissner's "Bericht über die Vortschritte der Anatomie und Physiologie," for 1859, that Hoppe had already observed this same optical property of the gastric fluid; and I willingly give up to him the priority of the discovery; at the same time it should be understood that Hoppe merely detected the bare fact, and only expressed an opinion on its cause, based on one experiment. He believed this phenomenon to be due to a substance secreted in the gastric juice, while I have shown that it is owing to a product of the digestion of animal food, or a *peptone*.

There are two different animal tissues, which, when submitted to the action of gastric juice, in or out of the body, yield polarising peptone—these are cartilage and the mucous tissue of boiled intestines, which can be easily separated from the muscular tissue. I could obtain none, or no appreciable quantity of this substance, from pure coagulated albumin or coagulated casein, when digested in gastric juice out of the body. My experiments on the digestion of meat out of the body, have failed to give me any clear results, although dogs fed exclusively on cooked beef-steaks for a week, invariably yielded a gastric fluid which acted on polarised light. We can be sure that the constituent of gastric juice which thus rotates the plane of polarisation of light, is a *peptone* and not a *substance secreted*; for if, after keeping a dog fasting for thirty

hours or longer, and then washing out his stomach thoroughly with water, the animal be made to swallow silicious pebbles, the small quantity of gastric juice secreted has no power of rotating the polarised ray. The result of this experiment is at variance with that obtained by Hoppe, who, after allowing an animal to fast, excited the gastric secretion with a glass rod, without however, taking the precaution of washing the stomach, and found that the fluid acted on polarised light. After exciting the secretion with fragments of bone, I obtained a gastric fluid which exerted but a very slight influence on polarised light, showing only seven divisions to the left in Soleil's saccharometer, while when the secretion was excited by cartilage, the rotation was from thirty to forty divisions, obviously from the digestion of the cartilage; and moreover, gastric juice, mixed with cartilage or with the internal tissue of boiled tripe, and exposed in a water-bath to a temperature equal to that of the body, acquires, after a short time, a power of deviating the plane of polarisation, which may be twice as great as that it possessed before the commencement of the artificial digestion.

After many experiments as to the best method of extracting from the gastric fluid the peptone under consideration, I succeeded in preparing it in a comparatively pure state, and then found it to be quite similar in its chemical properties to Lehmann's peptone. Four experiments were made with the dry substance in order to determine its rotatory power in Soleil's saccharometer. Solutions of the peptone in twenty-five cubic centimetres of water yielded for 1°, or division of the instrument, 0·020, 0·023, 0·027, 0·029 grammes: average 0·024 grm. Therefore, when gastric juice is examined in the saccharometer, for every degree of rotation to the left, the fluid contains 0·024 grm. of polarising peptone, or a proportion closely approximating to that, in twenty-five cubic centimetres.

Besides its office of transforming meat and allied articles of food into soluble substances, the stomach is possessed of another power no less important for the purposes of nutrition. I have discovered that it has the property of converting neutral fats, containing stearin, margarin, and butyrin, into their corresponding fatty acids; this fact, simple as it appears, is the key to the explanation of the digestion of fats. The fats of food are constantly neutral, they are not acidified by the process of cooking,

although heated even for a length of time in contact with the acid juice of flesh, and as fatty acids are found in the stomach, it must be owing to a phenomenon of gastric digestion. If a dog bearing a gastric fistula be made to eat butter, the fluid extracted through the fistula a quarter of an hour or twenty minutes later, or even less, will smell strongly of butyric acid. The fat of beef or mutton, after having remained for a certain time in the stomach, yields to alcohol, although not to water, an acid reaction. When the food taken contains but little fat, the whole of it, perhaps, is acidified during the gastric digestion; in those cases where much fat is ingested, I believe a part of it escapes from the stomach, without having undergone any change. With respect to the olein of food, I had concluded in a paper I communicated to the Royal Society, in 1858, that this substance is not acidified in the stomach, but I do not wish to be too positive regarding this statement.

The importance of the transformation of neutral fats into fatty acids in the stomach will be readily understood, if we take into consideration the action of bile upon these substances, the characteristic physiological property of that secretion being its power of converting fatty acids into an emulsion, while, with regard to neutral fats, it exhibits no such influence: consequently fats undergo in the stomach a certain transformation, by which means the bile becomes capable of acting upon them, and transforming them into an emulsion.

I must now beg to make a few observations on the phenomenon of fatty emulsions.

When neutral fats or fatty acids in a fused condition are agitated with water, no emulsion is formed, but large globules are seen to pervade the fluid; on standing they immediately run into each other, and rise to the surface, the aqueous fluid remaining perfectly clear. When fused *neutral fats* are agitated with a solution of neutral tribasic phosphate of soda, I have observed the same phenomenon to take place as with pure water, but when fused *fatty acids* are treated with a solution of phosphate of soda, an emulsion is formed, or in other words, the globules of fat lose the property of running into each other; they remain separate, the fluid assuming a milky appearance: consequently phosphate of soda does not act equally on neutral and on fatty acids. This subject appearing to me of great interest, I have given it much attention,

and I have found that the emulsion produced by acting on fatty acids with phosphate of soda is invariably accompanied by the formation of a certain quantity of soap; and a fact worthy of note is that the formation of soap persists, although, from the neutral phosphate becoming transformed into an acid phosphate, the emulsion is suspended in an acid fluid.

Emulsions of fat are also produced when bile and fused fatty acids are agitated together, or when pancreatic juice is shaken with both neutral or acid fats. This state of emulsion or of minute division of fats is indispensable for their absorption in the blood; an inquiry into the real nature of an emulsion would be therefore an object of much importance. Is it not something more than a mere mechanical division of fats into very small globules? I believe there are strong grounds for the assumption that there can be no emulsion without a chemical action, which may be conceived to take place in the following way:—When fused fatty acids are shaken in a test-tube with phosphate of soda or bile, the fat is instantly divided by a mechanical process into very minute globules, just as would happen if the fat was agitated with water; but at that moment each of these very small fatty particles becomes surrounded with a layer of soap, from the surface of the globule being saponified by the phosphate of soda or bile. From this circumstance the globules of fat lose their property of running into each other, and acquire a slight increase of specific gravity, which however is not sufficient to prevent them from rising slowly in the mother-liquor, and finally occupying the upper part of the liquid. Thus it is that the fluid is milky, and that the emulsion takes a much longer time to rise to the surface than pure oil would. The chemical analysis of the emulsion bears out this view, for I have found it to consist invariably of free fatty acid and soap.

This theory may have been already proposed without my knowledge; its adoption will assist in explaining the absorption of fats: for in this case, when in the form of an emulsion, they can no longer be in direct contact with the intestines, a layer of soap intervening between the fat and the membrane. Soaps may be conceived to pass through a membrane, whilst fat is known to be incapable of so doing, consequently we may imagine fats to be absorbed under the form of complex globules, the inside of which is free fat, and the outside soap.